

The University of Chicago

THE COEFFICIENT OF VISCOSITY OF HELIUM AND
THE COEFFICIENTS OF SLIP OF HELIUM AND
OXYGEN BY THE CONSTANT DEFLECTION
METHOD

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL
OF SCIENCE IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

BY
M. N. STATES

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ABSTRACT

Coefficient of viscosity of helium by the constant deflection method.—Using carefully purified He, which showed only a spectroscopic trace of H, six series of measurements at about 23° C gave $\eta_{23} = 1962.3 (10)^{-7}$. This is about 2 per cent less than values obtained by the capillary method, but is believed correct to within 0.1 per cent.

Coefficients of slip of helium and oxygen for polished and unpolished silver oxide surfaces.—The values obtained for $\zeta_{76} (10)^7$ are: for the unpolished surface, 123 (He), 61.1 (O); for the polished surface, 160 (He), 64.5 (O). These are probably accurate to one per cent. From Maxwell's equation, the values for complete diffuse reflection, which are the minimum values, are computed to be 191 (He) and 70 (O). The low experimental values suggest a "reverse-specular" reflection or perhaps the abnormal momentum transfer at the surface may be attributed to an excess of molecules leaving the cylinders due to the release of oxygen at low pressures. The change of the slip with time, observed in previous work, is shown to be due to the release of occluded gases, chiefly oxygen in the case of a silver oxide surface.

Increase in the stiffness of the steel suspension wire, noted by Van Dyke, continues.

INTRODUCTION

THE recent work of Stacy¹ and Van Dyke² on the coefficients of slip of air and carbon dioxide showed clearly that these quantities depend upon the nature of the bounding surfaces. The coefficient of slip was larger for the smoother surfaces, indicating that these reflected a greater number of molecules specularly. For old shellac (the "roughest surface" used), however, both of these observers found a nearly diffuse reflection for air; *i.e.*, the molecules were reflected or re-emitted from the surface at no favored angle. This conclusion is based on Maxwell's³ expression for the value of the coefficient of slip

$$\zeta = \frac{1}{2} \eta \sqrt{\frac{2\pi}{p\rho}} \cdot \left(\frac{2}{f} - 1 \right) \quad (1)$$

when a fraction f of the molecules is diffusely reflected and a fraction $(1 - f)$ is considered specularly reflected from the surface; their result

¹ Stacy, Phys. Rev. 21, 239 (1923).

² Van Dyke, Phys. Rev. 21, 250 (1923).

³ Maxwell, Scientific Papers 2, 708.

came out nearly equal to the value calculated for $f = 1$. This value corresponding to $f = 1$ should be the minimum possible value of the slip.

It was thought desirable to make a study of the coefficient of slip, using different surfaces and other gases, in order to test this minimum value further. In addition, the chemical composition of the surface used afforded an excellent opportunity for studying the "time effect" on the slip. Finally, the coefficient of viscosity of helium was determined.

THE APPARATUS¹

The constant deflection method was used, the apparatus being that with which Gilchrist² and Harrington³ determined the absolute value of the coefficient of viscosity of air. Such a complete description of the apparatus used in the above work has been given that it will be sufficient here to indicate only what changes have been made since the apparatus was used by Van Dyke.

A sliding pulley which fed the cord to the drum of the driving mechanism was eliminated and two ball bearing pulleys made from bicycle hubs were substituted for the two ordinary pulleys which carried the driving weights. These changes in the driving mechanism made a decided improvement in the constancy of the speed of rotation of the outer cylinder, as evidenced by the chronograph record, and a corresponding improvement in the steadiness of the deflection of the inner cylinder. Static charges, it was observed, produced a deflection of the inner cylinder, the steel suspension wire being attached to a glass tube which insulated the inner cylinder from the ground. Accordingly, as an added precaution, the entire inner system was grounded, although observations were not taken when such disturbing effects were present.

The brass cylinders were coated with a layer of silver oxide of the order of 0.001 mm in thickness which constituted the "first" surface. This layer was formed by the displacement of the metal in the brass by the silver in a solution of silver nitrate, the silver immediately oxidizing. The cylinders were rotated in the solution during this process so that a uniform coat was obtained. The deposit was allowed to dry thoroughly in air before the cylinders were set in place, and then stood about five months, for the most part at low pressure, before the first observations

¹ It is interesting to note that A. Timiriazeff used an apparatus somewhat similar to the above for coefficient of slip and viscosity determinations. For slip determinations he used pressures of the order of .001 mm of mercury and calculated his results in a slightly different manner. His values for the coefficients of viscosity for air, carbon dioxide, and hydrogen are from eight to fifteen per cent higher than those obtained by other observers. *Ann. der Phys.* 40, 971 (1913).

² Gilchrist, *Phys. Rev.* 1, 124 (1913).

³ Harrington, *Phys. Rev.* 8, 738 (1916).

here recorded were taken. A second set of observations was taken for the coefficient of slip after the oxide had been burnished with paper and polished with chamois.

The evacuating system consisted of a mercury diffusion pump supported by a May-Nelson pump. The latter was thoroughly over hauled, the tubes leading from the pumps being enlarged so that the time of evacuation was considerably reduced. In the case of helium a complete set of data for the determination of the value of the coefficient of slip could be obtained within twenty minutes after the gas was introduced into the apparatus. Stacy, using a Gaede pump, was able to take similar observations only after two hours of pumping. Van Dyke, however, in the latter part of his work reduced this time to one hour for slip determinations at a pressure of about 0.1 mm of mercury. After it was found that the slip determinations here recorded plotted against time gave a straight line parallel to the time axis, no special effort was made to hurry the evacuation.

The constant temperature room was kept close to 23° C by means of an electric heater controlled by an ether thermostat. The temperature within the apparatus was read on a Beckmann thermometer which was compared with a standard Baudin thermometer before and after this series of data was taken. The Beckmann showed no change in calibration in this period of five months. With a fan constantly circulating the air in the room, the variation of the temperature within the apparatus was of the order 0° 0.02 C during a run of about thirteen minutes and often no change in the Beckmann could be detected in this interval although it read directly to one hundredth of a degree.

It is interesting to note the continued increase in the stiffness of the steel suspension wire previously noted by Van Dyke. The suspension used was the "F" suspension of Harrington. The record of this change, indicated by the decreasing period, is as follows:

Harrington.....	175.58 sec.
Stacy.....	175.48 "
Van Dyke (Nov. 1920).....	175.45 "
" " (June 1921).....	175.42 "
States (April 1922).....	175.25 "

EXPERIMENTAL PROCEDURE

In a preceding paper Van Dyke has given the working equations and the general experimental procedure for the determination of the coefficients of viscosity and slip by the constant deflection method. It will be sufficient, therefore, to indicate the departures from this method.

Prior to the first slip work on oxygen the apparatus was allowed to stand several days at a pressure in the neighborhood of 0.001 mm of mercury after which it was bathed out and oxygen admitted to the chamber. Several determinations of apparent viscosity were made at about 6.5 cm of mercury. These were corrected for slip. The apparatus was then evacuated to a lower pressure, several apparent viscosity runs taken, which together with the mean of the former readings yielded values of ζ_{76} . The pumping was continued and more slip determinations made at this lower pressure. The process was continued until pressures were reached at which the mean free path of the molecules became comparable with the distance between the cylinders where the equations referred to do not hold. (See Tables I. and II.) The same method was

TABLE I. Oxygen—First Sample. Coefficient of Slip—Unpolished Oxide Surface

$$\eta_{23} = 2035.8 \times 10^{-7}, \quad k' = 8.1879 \times 10^{-7}, \quad k = 2.814$$

T = time from initial pumping to end of run

t (sec)	d (cm)	$\theta^\circ \text{ C}$	p (mm)	$(\eta_0/\eta_p - 1)$ $\times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.394	77.954	22.826	0.274	48.9	62.7	1
30.442	77.872	22.805	0.274	48.3	61.9	1.33
30.416	77.991	22.820	0.274	47.7	61.1	1.75
30.430	77.993	22.985	0.277	47.6	61.7	18
30.415	78.090	23.100	0.278	47.2	61.4	18.5
30.426	76.746	23.200	0.196	65.4	60.0	19
30.413	76.717	23.040	0.196	65.8	60.3	23
30.389	76.847	23.107	0.196	65.0	59.6	23.5
30.394	76.527	22.820	0.196	68.4	62.7	41.5
30.388	76.579	22.859	0.196	68.0	62.3	42
30.401	76.552	22.795	0.196	67.7	62.1	46
30.400	76.619	22.839	0.196	67.0	61.4	46.5
30.388	76.834	23.204	0.196	65.5	60.0	61.0
30.382	76.735	23.192	0.196	67.1	61.5	61.5

Mean $\zeta_{76} = 61.3 \times 10^{-7}$

used in getting the viscosity of helium, the pressure being 10 cm of mercury instead of 6.5 cm. In the slip determinations, however, in order to save the helium, the gas was withdrawn after the viscosity runs by means of a Toepler pump, and then small quantities of helium were re-introduced into the apparatus for the low pressure observations. The method used on oxygen was tested and yielded the same value for the slip as the latter method. Furthermore, re-introducing the helium gave the same value of the coefficient of viscosity, which justified the use of the same value of η_0 for all slip computations. (See Tables III. and IV.) The slip observations for the polished oxide surface were taken

TABLE II. *Oxygen—Second Sample. Coefficient of Slip—Unpolished Oxide Surface*

$$\eta_{23} = 2037.4 \times 10^{-7}, \quad k' = 8.1879 \times 10^{-7}, \quad k = 2.814$$

t (sec)	d (cm)	$\theta^\circ \text{ C}$	p (mm)	$(\eta_0/\eta_p - 1)$ $\times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.471	78.827	22.794	0.372	35.4	61.6	4.25
30.438	78.908	22.810	0.372	35.5	61.8	4.5
30.394	78.468	23.045	0.297	43.5	60.4	6.5
30.406	78.423	23.052	0.297	43.7	60.7	7.0
30.374	78.504	23.008	0.297	43.6	60.6	10
30.392	78.466	23.039	0.297	43.6	60.6	10.5
30.362	77.257	23.030	0.211	60.9	60.1	11.5
30.301	77.394	23.000	0.211	61.1	60.3	12
30.238	74.806	23.280	0.128	100.9	60.4	29.5
30.238	74.808	23.224	0.128	100.7	60.3	30
30.270	71.070	22.775	0.0848	155.9	61.8	52.5
30.248	71.184	22.742	0.0852	154.9	61.7	53

$$\text{Mean } \zeta_{76} = 60.9 \times 10^{-7}$$

in the same manner, with the exception that the apparatus was not allowed to stand at low pressures more than twenty-four hours but was evacuated to 0.0007 mm of mercury before the gas was introduced.

TABLE III. *Viscosity of Helium—Unpolished Oxide Surface*

$$p = 10.0 \text{ cm}, \quad k' = 8.1879 \times 10^{-7}$$

t (sec)	d (cm)	$\theta^\circ \text{ C}$	$\eta_\theta \times 10^7$	$\eta_{23} \times 10^7$
30.482	78.554	22.790	1960.6	1961.6
30.450	78.654	22.820	1961.0	1961.8
30.462	78.635	22.875	1961.3	1961.9
30.476	78.593	22.890	1961.2	1961.7
30.541	78.421	22.890	1961.0	1961.5
30.512	78.520	22.902	1961.6	1962.0

$$\text{Mean } \eta_{23} = 1961.8 \times 10^{-7}$$

$$\text{Corrected for slip, } \eta_{23} = 1962.3 \times 10^{-7}$$

Instead of making an absolute determination of the coefficient of viscosity, several observations were made on the values of t the period of rotation, and d the corresponding deflection for air, just after the work on helium, and the value of $k' = \eta/t\dot{d}$ was calculated assuming the value of η_{23} for air to be 1822.6×10^{-7} , as determined by Harrington. The mean value of eight such observations gave $k' = (8.1879 \pm 0.0018) \times 10^{-7}$. The value of k' obtained some months before came out 0.1 per cent lower. This change was probably due to the decrease in the period of vibration of the inner cylinder which was of the order of one part in two thousand and effective in increasing k' by one part in one thousand. On account of this shift, the k' determined just after the helium runs

TABLE IV. *Helium. Coefficient of Slip—Unpolished Oxide Surface* T' = time from introduction of gas to end of run

$$\eta_{23} = 1962.3 \times 10^{-7}, \quad k' = 8.1879 \times 10^{-7}, \quad k = 2.814$$

t (sec)	d (cm)	$\theta^\circ \text{ C}$	p (mm)	$(\eta_0/\eta_p - 1)$ $\times 10^3$	$\zeta_{76} \times 10^7$	T' (hr)
30.314	77.703	23.173	1.50	17.9	126	0.5
30.290	77.744	23.150	1.50	18.1	127	1.0
30.234	77.861	22.942	1.50	17.9	126	5
30.257	77.802	22.960	1.50	18.0	126	24
30.208	77.386	22.920	1.05	25.0	123	0.33
30.185	75.574	23.087	0.518	50.8	123	0.6
30.175	75.715	23.150	0.518	49.4	120	1
30.284	75.383	23.043	0.520	49.9	121	18.5
30.230	74.741	22.910	0.435	60.5	123	1.25
30.244	74.816	22.975	0.435	59.1	120	2
30.297	73.367	23.070	0.333	78.4	122	25
30.211	73.511	23.032	0.333	79.0	123	48

$$\text{Mean } \zeta_{76} = 123 \times 10^{-7}$$

was used in getting the value of the coefficient of viscosity of helium. In fact this value was used throughout the first work as the value of the slip is independent of k' . Another determination of k' was made after the oxide surface was polished and the cylinders re-set. The mean of six observations gave $k' = (8.1933 \pm 0.0015) \times 10^{-7}$.

TABLE V. *Oxygen. Coefficient of Slip—Polished Surface*

$$\eta_{23} = 2036.0 \times 10^{-7}, \quad k' = 8.1933 \times 10^{-7}, \quad k = 2.814$$

t (sec)	d (cm)	$\theta^\circ \text{ C}$	p (mm)	$(\eta_0/\eta_p - 1)$ $\times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.384	77.438	23.060	0.250	56.3	65.7	1.5
30.384	77.477	23.062	0.251	55.8	65.7	2
30.344	75.732	23.078	0.170	81.5	64.9	3
30.326	73.759	23.155	0.121	112	63.5	3.5
30.223	71.197	23.160	0.0865	156	63.2	4
30.217	71.243	23.140	0.0884	155	64.2	4.5

$$\text{Mean } \zeta_{76} = 64.5 \times 10^{-7}$$

The temperature corrections were made using the following approximate formulæ for small variations in temperature about 23° C , the last two deduced from Sutherland's equation.

Air

$$\eta_\theta = \eta_{23} + 4.93(\theta - 23) \times 10^{-7}. \quad (2)$$

Oxygen

$$\eta_\theta = \eta_{23} + 5.54(\theta - 23) \times 10^{-7}. \quad (3)$$

Helium

$$\eta_\theta = \eta_{23} + 4.70(\theta - 23) \times 10^{-7}. \quad (4)$$

TABLE VI. Helium. Coefficient of Slip—Polished Surface

$$\eta_{23} = 1962.3 \times 10^{-7}, \quad k' = 8.1933 \times 10^{-7}, \quad k = 2.814$$

t (sec)	d (cm)	θ° C	p (mm)	$(\eta_0/\eta_p - 1)$ $\times 10^3$	$\zeta_{76} \times 10^7$	T' (hr)
29.911	78.486	22.982	1.74	20.1	164	0.33
29.840	78.673	23.038	1.74	20.3	165	0.75
30.484	76.909	22.858	1.62	21.2	161	17
29.952	78.303	23.102	1.60	21.4	160	0.5
29.985	78.242	23.130	1.60	21.2	159	1
30.431	76.394	23.146	1.11	30.6	159	2
30.392	76.489	23.145	1.11	30.6	159	2.5
30.370	74.398	23.155	0.552	60.4	156	3
30.253	72.634	22.895	0.373	89.7	157	19
30.080	73.071	22.915	0.373	89.4	156	19.5

$$\text{Mean } \zeta_{76} = 160 \times 10^{-7}$$

The constant for oxygen is Sutherland's value; that for helium is Schmitt's. The Eq. (2) is the one used by Prof. Millikan.¹

THE GASES

Oxygen.—The oxygen for the coefficient of slip determinations was obtained by heating potassium permanganate. The flask containing the permanganate was heated a number of times and after each heating the flask and connecting tubing was exhausted to the point where a discharge passed outside rather than through a Geissler tube. The heat drove out the occluded gases from the flask and at the same time the liberated oxygen washed out the auxiliary apparatus. Heat was then applied and the oxygen produced was admitted to the large volume enclosing the cylinders through a coil made from a meter and a half of tubing in series with two traps, all at liquid air temperatures. This process gave quite pure oxygen, free from carbon dioxide and moisture, but showing hydrogen as an impurity when examined by a spectroscope using a disruptive discharge. However, the gas gave a coefficient of viscosity only 0.3 per cent lower than the value obtained by Yen² on the same apparatus when very pure oxygen was used. In view of this, and coupled with the fact that η_{23} for hydrogen is about one third of η_{23} for oxygen, little hydrogen could have been present. Furthermore, one would expect slight impurities not to affect the value of the coefficient of slip in as much as the determining quantity is a ratio of two apparent coefficients of viscosity of the same gas at different pressures, the percentage of impurities being nearly constant. Within the limit of experimental error, the values of the coefficient of slip (unpolished oxide surface)

¹ Millikan, Ann. der Phys. **41**, 759 (1913).

² Yen, Phil. Mag. **38**, 582 (1919).

of the two samples of oxygen are the same, although the viscosities of the two samples differ. This seems to justify the assumption that slight impurities do not affect the coefficient of slip.

Helium.—The helium, approximately 97–98 per cent pure, was obtained from the laboratory supply. The chief impurities were nitrogen, oxygen, hydrogen, neon and possibly some hydro-carbons. This gas was circulated through charcoal tubes at liquid air temperatures by means of a Toepler pump, a process which removed most of the impurities. A copper oxide tube removed the hydrogen. This purified gas, examined with a spectroscope and under a disruptive discharge, showed a trace of hydrogen and neon at favorable pressures. Collie and Ramsay¹ found that 0.001 per cent of hydrogen was visible in helium at all pressures and obtained similar results for inert gases in helium. Gille² found that one per cent of hydrogen lowered the viscosity of helium less than one per cent. In this instance there could be no such amount present. In view of this, the slight trace of hydrogen and neon present would introduce a negligible error. It might be stated that the process of purification was continued until no change in the viscosity was apparent, and that the last set of readings is given in Table III. The values just previous to these, in which a change was noted, indicated that neon was the last impurity taken up by the charcoal.

DISCUSSION

The value of the coefficient of viscosity of helium here recorded is lower than that usually quoted. Determinations by the capillary tube method, however, generally yield values somewhat higher than those obtained by the constant deflection method. The ratios of values of viscosity usually come out about the same. In this instance the ratios disagree by nine parts in one thousand. Using Harrington's value of air, we have $\eta_{23}(\text{He}) = 1.077 \eta_{23}(\text{air})$. Shultz³ using the capillary tube method got $\eta_{15}(\text{He}) = 1.086 \eta_{15}(\text{air})$, which ratio would not be materially changed at 23° C in as much as the temperature coefficients of the two gases are nearly the same. Rankine⁴ using a modified form of the capillary tube method got $\eta_{9.8}(\text{He}) = 1.078 \eta_{9.8}(\text{air})$. After making an approximate slip correction his value agrees with Shultz's. Shultz's value of the coefficient of viscosity of helium at 15° C, reduced by the Sutherland formula, gives $\eta_{23}(\text{He}) = 2006 \times 10^{-7}$.

In spite of this the writer feels justified in claiming a high degree of

¹ Collie and Ramsay, Roy. Soc. Proc. **59**, 257 (1896).

² Gille, Ann. der Phys. **48**, 829 (1915).

³ Shultz, Ann. der Phys. **6**, 302 (1901).

⁴ Rankine, Roy. Soc. Proc. **83**, 516 (1910).

precision for the value of the coefficient of viscosity of helium obtained. The method itself is generally considered to be superior to the capillary tube method. A statement as to the purity of the gas has already been made. Finally, from the small probable error in the mean value of k' and from the consistency in the values of η_{23} for helium, it would appear that the value quoted is as nearly correct as Harrington's value of η_{23} for air. The error in Harrington's work is probably not more than 0.1 per cent.

As has been pointed out, the coefficient of slip is essentially a difference between two measured physical quantities, each of which involves an error of the order of 0.1 per cent. When this difference is small, the error in the value of the slip may amount to several per cent. On the other hand, when the difference is large, the error mentioned would be small, but since the pressure for one of the readings would have to be low, the value of the slip coefficient would be unreliable, for at low pressures the free path becomes comparable with the distance between the cylinders. For this reason the slip determinations here recorded were taken within a range of pressures where the two effects taken together would introduce the least distortion. The range of pressures for oxygen was between 0.37 mm and 0.08 mm of mercury. For helium, the free path being approximately three times that of oxygen, the range of pressures was shifted to values about three times as high. The mean of the coefficients of slip within this limited range should be correct to within one per cent.

The fact that the "time effect" was not observed in the slip work is largely responsible for the consistency in the values of ζ_{76} . Stacy and Van Dyke usually disregarded readings after the first hour or two, due to the *rise* in slip. This increase was attributed to the release of occluded gases of low viscosity. In trying out the silver oxide with air, the "time effect" was marked, but in the *reverse* direction. Silver oxide was found to give off oxygen at low pressures which would account for this decrease. In order to make sure that this was the true cause of the "time effect," a study was made of the coefficient of slip of oxygen, which ought to remain constant with time upon the above hypothesis. Tables I., II., and V. indicate slight changes in pressure but constant values of the slip, which seems to verify the contention. In view of this, the mean value of ζ_{76} is probably equal to the value of the coefficient of slip at zero time.

In helium no "time effect" was observed. This may be due to the fact that the coefficients of viscosity of helium and oxygen are nearly the same. Before the first helium runs were taken, however, the apparatus stood for a month at a pressure of about 0.001 mm of mercury. In the later slip work, the apparatus stood at low pressures for about 24 hours

and, as before stated, was evacuated to a pressure of the order of 0.0007 mm of mercury before the helium was introduced; consequently over a range of pressures from 1.7 mm to 0.33 mm of mercury one might not expect the release of oxygen. A combination of these two effects may account for the consistency in the values of ζ_{76} .

The coefficients of slip of oxygen and helium obtained are considerably lower than any values which might be expected from Maxwell's expression for slip. The minimum value given by Eq. (1) would be obtained by imposing the condition of diffuse reflection; *i.e.*, placing $f = 1$. Whence ζ_{76} for oxygen = 70×10^{-7} and ζ_{76} for helium = 191×10^{-7} . The viscosities of oxygen and helium are so high in comparison with the viscosities of gases or vapors which might reasonably be expected to enter as impurities at low pressures that lowering of the slip through an increase of viscosity seems improbable. The observations seem to indicate no measurable change in slip over intervals as long as sixty hours, which would hardly be expected if there were changes in the character of the gas at low pressures. Turning to surface conditions, diffuse reflection would mean that the entire tangential component of the momentum per second due to the streaming velocity of the molecules is communicated to the surface. A lower value of the slip could arise only when a larger tangential force exists at the surface. This condition would be satisfied if a part of the molecules striking the surface rebounded with a component of velocity opposite to the general streaming velocity, the remainder of the molecules being assumed diffusely reflected. This abnormal tangential force also suggests an increased density at the bounding surface, the excess molecules being furnished by the oxide surface. This would tend to diminish the streaming velocity of the surface layer and thereby increase the force at the surface of the cylinders.

In conclusion, the writer wishes to thank Professor R. A. Millikan for suggesting this further study of the slip, and Professor H. G. Gale and other members of the staff at Ryerson for helpful suggestions and assistance in various phases of the work, especially in the purification and analysis of the gases.

RYERSON PHYSICAL LABORATORY,
CHICAGO UNIVERSITY,
July 26, 1922

